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(56) Documents Cited
EP 0473952 A2 **EP 0373286 A1** **US 5277857 A**
US 4336828 A

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(54) Abstract Title
Cellulose food casing

(57) A cellulose food casing comprises at least a region which is formed from an extruded cellulose solution having incorporated therein an optical property modifier to impart colour, shine and/or lustre to the said region. The optical property modifier is preferably a particulate material such as a pearlescent pigment or solid or hollow delustering beads. The cellulose solution may be a cellulose-NMMO dope (where NMMO is N-methylmorpholine N-oxide). The casing is optionally self-supporting, and/or reinforced. The casings may be tubular food casings wherein the optically modified regions of are arranged in annular sections, longitudinal parallel stripes or helical stripes. A process for manufacturing an optically modified cellulosic food casing is also disclosed.

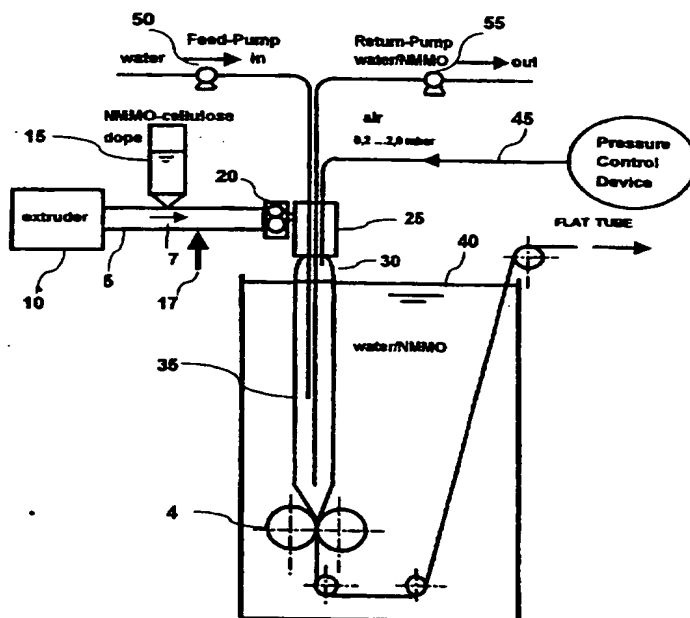


Fig.1

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

The claims were filed later than the filing date but within the period prescribed by Rule 25(1) of the Patents Rules 1995.

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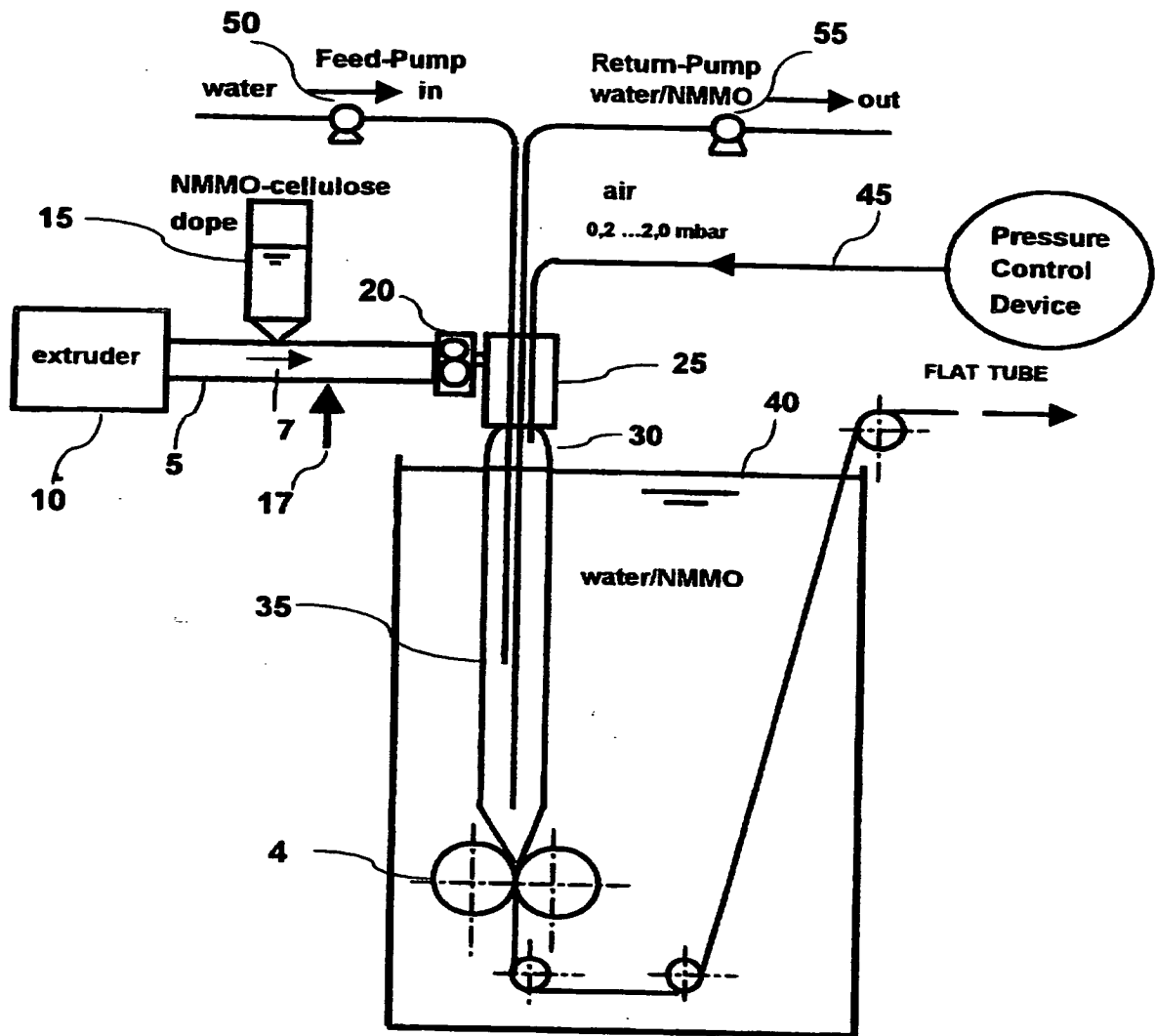


Fig.1

CELLULOSE FOOD CASING

The present invention relates to shaped cellulose bodies such as pigmented cellulose food casing, in particular pearlescent pigmented, and/or delustered
5 cellulose food casing.

It is well known that cellulose food casings are used in producing stuffed or wrapped foods such as sausages and the like. Such casings may be produced by utilising either the viscose process or the NMMO (N-methylmorpholine N-
10 oxide) process. Casing may be produced as a continuous seamless tube or as flat film. Such film may be folded around a food product to give a wrapped food product or the film edges may be joined to give a tube with a longitudinal seam.

15 The viscose process is well known and currently is the most common method used for producing cellulose casing. For a brief discussion of this process see for example the introductory portion of US Patent, No. 5,277,857. Briefly, the viscose process involves making a solution of the
20 sodium xanthate salt of cellulose and extruding this chemically derivatised cellulose solution into a coagulating and regenerating bath to form regenerated cellulose as a continuous tube.

The NMMO solution process however is gaining useful
25 recognition as an alternative for forming cellulose articles such as sausage casings. This process does not

chemically derivatise the cellulose, but instead involves cellulose dissolution in the NMMO solvent to form a solution known as a dope.

Briefly, the NMMO cellulose dope is made as follows.

5 Cellulose pulp is mixed with NMMO which contains about 50% water; reduced pressure and heat are then applied so that the mixture boils at about 70°C. At about 12% water content in relation to the amount of NMMO, the NMMO forms a mono-hydrate and the cellulose then fully dissolves to form the

10 dope on increasing the temperature to 95°C. Stabilisers are added to reduce degradation and discolouration of the cellulose end product. Further reduction of pressure removes any air bubbles from the dope which, at about 100°C, is a visco-elastic melt having high viscosity compared to

15 viscose and a pronounced elastic behaviour. This procedure takes approximately 3 hours using laboratory equipment starting from the cellulose pulp/NMMO mixing stage. It is believed that the time period may be reduced to less than one hour by using industrial scale equipment. The dope is

20 solid at room temperature (about 25°C) and can be ground into pellets ready for feeding into a screw extruder. These pellets can be stored for a considerable length of time without showing negative effects on the extrusion process.

25 Sausage casings may be formed by extruding melted dope through an annular die orifice and passing the tubular

cellulose solution extrudate into a precipitation bath containing water or a solution of NMMO in water. A positive pressure applied to the inside of the freshly extruded tube causes the tube to remain open, that is inflated. This extrusion method is known as blown extrusion and when the tube is drawn through the bath by nip rolls results in oriented biaxially stretched tubes. Furthermore provision is made for the precipitation liquid to fill the inside of the tube. The precipitation liquid is a non-solvent for cellulose and a solvent for NMMO. The cellulose thus precipitates to form a solid cellulose semi-gel tube. This tube is processed further to remove any remaining NMMO, and can be treated with a plasticising agent prior to drying. A description of the NMMO cellulose solution process has been described in for example US Patent No. 5,277,857.

The NMMO cellulose solution process is gaining popularity as a potential method for producing cellulose food casings because of significant cost savings and safer or less damaging environmental aspects. For example, unlike the viscose process, toxic carbon disulphide is not used in the NMMO process. Also corrosive chemicals such as sodium hydroxide and sulfuric acid are not used. Furthermore the NMMO solvent can be recycled resulting in NMMO recoveries of up to 99.5%.

Notwithstanding the aforementioned advantages of the

NMMO process, undesirable effects such as partial cellulose depolymerisation and degradation can occur on prolonged heating of cellulose-NMMO dope. Depolymerisation gives shorter polymer chains, and cellulose casings made from partially depolymerised cellulose may have a reduced strength. Furthermore, degradation of cellulose in the initially, substantially colourless dope can result in the dope becoming undesirably coloured. This colouration can persist, that is, may not be removed during the casing formation processes. These cellulose casings may therefore have an unappetising or unappealing appearance.

It is an object of the present invention to obviate or mitigate the abovementioned disadvantages, in particular to provide a cellulose casing which possess an aesthetic or appealing appearance.

According to a first aspect of the present invention there is provided a shaped body comprising cellulose and wherein said body is designed such that it has modified optical properties.

It is to be understood that the term optical properties refers principally to the visual appearance of the food casing, that is its interaction with visible light for example, by absorption, refraction and reflection. Particularly relevant is the colour of such a casing, or other appearance, such as degree of shine or lustre. The term optical properties however may also be taken to

include any interaction of the casing with electromagnetic radiation, such as for example ultra violet light, infra red radiation or x-rays. The term "modified" is used in the sense that the optical properties of the casing have been altered through modification of the casing either during and/or after its manufacture. For example a modified casing could be made by modifying an existing, pre-made casing or alternatively through modification of the casing precursor material such as the cellulose-NMMO dope.

Particularly suitable types of food casing to which the present invention may apply are those formed from cellulose, either as regenerated cellulose from for example the viscose process, or reformed cellulose from a true solution process such as the cellulose-NMMO process. Casings formed from either of these two processes may be termed self supporting because the major component is cellulose. Other types of cellulose casing to which the present invention may apply include the so-called fibrous casings. Different from self supporting casings, these casing types are reinforced, and comprise for example a cellulose permeated paper material such as a paper web. The paper component provides strength to the casing. These casings are formed by contacting a cellulose solution or viscose solution to a paper or paper like material and, following absorption of the cellulose solution by the paper

or paper-like material, precipitating or regenerating the cellulose within the fibrous matrix of the paper or paper like material. The cellulose and the fibrous matrix provide mutual strength reinforcement to the finished casing product.

Reinforced casings may be coloured by use of coloured paper webs or alternatively by using non-coloured paper and coloured viscose or cellulose dope to be absorbed by the paper. A combination of coloured paper and coloured viscose or dope may also be used.

With regard to the cellulose-NMMO solution process as previously mentioned the degree of degradation of solubilised cellulose can be controlled by using stabilising agents. Some of these agents are believed to control free radical depolymerisation processes which lead to discoloured cellulose dope solutions. Undegraded dope gives substantially non-coloured cellulose casings which are particularly suitable for colour to be imparted thereto.

Although cellulose dope solutions are generally non-coloured, colouration may occur for example through variations in the type of cellulose used. For example, different types of wood may give cellulose types which result in differently coloured dopes, and impurities, either themselves coloured or those which cause colouration, may be introduced by using materials which are

outside the usual specification parameters. Also, even in the presence of stabilising agents prolonged heating of the dope could give a coloured dope. Coloured dopes such as those described above, although being physically acceptable in every processable respect for forming food casings, may be unacceptable because of an unappetising final appearance of the casing, or simply because of an appearance which falls outside that usually encountered by customers. Under such circumstances it would be desirable for the casing manufacturer to change the casing colour to give an appearance which is acceptable to the casing purchaser or end user. This would allow coloured dopes to be used which would not normally be acceptable, thus reducing wastage of casing materials or limit further processing to remove unwanted colouration.

Incorporation of particulate material into a cellulose food casing is a preferred method of modifying the optical properties thereof. Particular application is found in true cellulose solution processes such as the NMMO process. Any suitable method can be used to incorporate the particulate material, for example, by mixing the material with the cellulose and/or cellulose solvent, for example NMMO, or alternatively by adding the particulate material to the completely solubilised cellulose-NMMO mixture. Still further, the particulate material may be added into an extruder concurrently with the solid cellulose-NMMO dope

pellets, granulate or powder, or may be added downstream of the dope entry port of the extruder by means of a second or side entry port. This method would thus introduce the particulate material into the partially or fully melted dope contained within the extruder.

Optically modified cellulose casings may also be made using a co-extrusion technique. This involves the use of two or more media which are to be extruded, for example two or more cellulose-NMMO dope solutions. Co-extrusion can be used to provide a di-functional tubular casing. For example a coloured cellulose-NMMO dope solution can be extruded simultaneously with a non-modified cellulose-NMMO dope solution. If a tubular casing is being produced arrangements can be made so that the modified solution forms the portion on the outside of the casing. If a coloured casing is produced by this method considerable savings in cost may be made because less pigment may be needed to give the desired colouration. Other specifically configured dies may be used to achieve other co-extrusion effects, for example striped casings may also be produced using co-extrusion.

Suitable particulate materials are those which are able to withstand the melt extrusion process conditions, for example exposure to temperatures in excess of about 110°C for the time the dope is resident in the extruder. These conditions should preferably not adversely affect the

physical characteristics of the particulate material. Particularly desirable is the maintenance of particle shape and colour.

5 A further desirable aspect of such particulate materials when applied to the present invention is chemical inertness or resilience to change by for example action of light, oxygen, the cellulose solvent, particularly NMMO, or other additives which may be present in the cellulose solution or the precipitation liquid, the precipitation
10 liquid itself, plasticising agents, oils or humectants used in casing manipulation or sausage manufacture. Furthermore, the particulate material should preferably not be soluble in any of the abovementioned substances. However, it may be desirable in some instances to use
15 particulate material in which the particular shape and/or colour thereof alters in a desirable manner on exposure to the processing conditions, such as the abovementioned temperature conditions or substances.

20 Particularly desirable particulates are those that impart colour to the final cellulose food casing. Particularly desired are pearlescent pigments which impart a pearl-like colour and shine to the casing. Pearlescent pigments are known materials and, without wishing to be limiting, are generally made of a thin metal oxide film
25 deposited on plate-like substrate particules. A relatively detailed description of pearlescent pigment action, effects

and properties can be found in the article by J. Carroll and K. Dyer, Modern Plastics, January 1999, page 86. A pearlescent colouration is made up of a multitude of colours which interact to give a distinctive colouration effect. The observed colour of materials coloured by pearlescent pigments depends amongst other things on the angle of observation relative to the surface of the material. Such aesthetic colouration can be particularly pleasing to an end user.

Still further, particulate materials may be used to alter the colour of degraded cellulose dope. Such dope is typically yellow or brown, often dark brown in colour. Such dope may give unacceptably coloured food casing and therefore addition of some particulate materials to the degraded dope, rather than modifying the colouration by imparting a further colour to the finished cellulose casing, may absorb such colour by, for example absorption of the coloured material or impurity present in the dope.

A further use of particulate materials in food casings relates to lustre control, that is the degree of brightness or shine of the casing. The lustre of casings according to the present invention may be changed in the absence of or in combination with a colour change imparted by for example a pearlescent pigment. Such lustre alteration can be accomplished by use of solid or hollow beads which may or may not be spherical having a typical diameter of 0.25 to

10.0 micro metres. Such beads, on incorporation into a food casing material tend to delustre or dull the casing. Such delustring tends to give a less shinny casing, that is, wherein the reflected light is more diffuse. Suitable delustring beads are hollow and may be made from an organic silicone polymeric material. Other polymeric materials may also be used. Such hollow beads are typically water permeable and allow water to move in both directions between the inside and outside of the bead through the bead wall.

As indicated above the pearlescent pigments or delustring beads can be mixed with the cellulose-NMMO dope in any suitable manner such as described herein before for particulate pigments. A particularly suitable method is to add the pearlescent pigment or delustring beads to the pre-formed liquid cellulose dope prior to extrusion.

According to a second aspect of the present invention there is provided a process for manufacturing an optically modified shaped cellulose body which comprises a particulate material comprising the steps of

- providing a derivatised or non-derivatised cellulose solution;
- adding a particulate material to said solution to form a dispersion of particles in said solution; and
- extruding said solution through a die orifice.

It should be noted that the processing conditions may

be chosen so that the cellulose body, for example a tubular sausage casing, comprises pigmented and non-pigmented regions. For example the casing may comprise annular sections of pigmented material alternating with non-pigmented annular sections. Alternatively the casing may comprise one or more longitudinal stripes of pigmented material and these stripes may be substantially parallel to non-pigmented longitudinal striped regions or may be helically arranged.

Embodiments of the present invention will now be described by way of non-limiting example, with reference to Figure 1 which shows a schematic representation of a NMMO - cellulose dope processing apparatus for providing tubular cellulose casings.

The apparatus comprises an extruder 10 which is typically a screw extruder, a die 25, water supply and water return means designated 50 and 55 respectively, and pressure control means 45.

The NMMO-cellulose dope is contained in a feed hopper 15 which is situated on the extruder screw shaft 5. The shaft 5 and die 25 are heated to about 100° C. The dope is typically used as solid pellets or granules and passes through an entry port into the extruder shaft, where it then melts. The melted dope is simultaneously mixed and transported along the extruder shaft 5 by the action of the turning screw (no shown). The melted dope travels along

the shaft 5 in the direction indicated by arrow 7 and passes through a filter screen (not shown) to a gear metering pump section 20. The optical modifying agents may be added to the dope during its preparation stage so that modified dope may be added to the hopper 15 and extruded directly. However further methods of adding the optical modifying agents may be used and a particularly convenient method involves adding an optical modifying agent downstream of the hopper 15 at a general position along the shaft 5 indicated by arrow 17. This entry position should be downstream of the filter screen if the optical modifying agent is a particulate material which may be trapped by the filter. The dope and modifying agent are together resident in the extruder shaft 5 for a time sufficient for their intimate admixture prior to extrusion through die 25. An annular die is used to give seamless tubular film. The die is positioned above a bath containing a precipitation liquid which is usually water at a temperature of 10°C - 20°C.

The freshly extruded dope is allowed to pass into the water bath 40 whereupon the cellulose precipitates to give a solid semi-gel tube 35. The tube 35 is pulled through the bath by nip rolls 4. Water is provided to the inside of tube 35 by a conduit and feed pump 50 so that the cellulose also precipitates at the interior of the tube.

During precipitation of the cellulose some NMMO will

dissolve in the water to give a dilute aqueous solution of NMMO. This solution is withdrawn from the tube interior via a conduit and pump 55, and replaced with fresh water via the conduit and pump 50. This water replenishment ensures effective cellulose precipitation. The portion, 30, of extrudate positioned between the die and precipitation bath is pressurised internally with a pressure of between 0.2 - 2mbar above atmospheric pressure supplied via pressure control means 45. This extrusion process gives an oriented biaxially stretched tube. Minor amounts of optical modifying additive may enter the water/NMMO mixture during precipitation. This material need not be wasted and can be readily recovered and reused at the addition stage during the first stages of the extrusion process. The water/NMMO precipitation bath mixture is further processed to recover the dissolved NMMO which is then used to prepare further quantities of cellulose-NMMO dope. It is possible to achieve NMMO recoveries of up to 99.5% which represents excellent conservation of material.

Further embodiments of the invention may be envisaged without departing from the inventive concept. For example optical modifying agents may be coated onto a cellulose casing after the casing has been extruded, alternatively a casing may be soaked or treated with an optical modifying agent such that the agent is absorbed into the casing.

CLAIMS

1. A cellulosic food casing, at least a region of which is formed from an extruded cellulose solution having incorporated therein an optical property modifier to impart a colour, shine and/or lustre effect to said region which is different from a colour, shine and/or lustre effect of a region formed from a cellulose solution having no optical property modifier incorporated therein.
2. A cellulosic food casing according to claim 1 wherein said optical property modifier is a particulate material which is substantially insoluble in said cellulose solution.
3. A cellulosic food casing according to claim 1 or claim 2 wherein said cellulose solution comprises a cellulose-NMMO dope.
4. A cellulosic food casing according to claim 2 wherein said particulate material comprises a pearlescent pigment.
5. A cellulosic food casing according to claim 2 wherein said particulate material comprises solid or hollow delustering beads.

6. A cellulosic food casing according to claim 5 wherein said beads have a diameter of 0.25 to 10.0 micrometres.
- 5 7. A cellulosic food casing according to claim 6 wherein said beads comprise an organic silicone polymeric material.
- 10 8. A cellulosic food casing according to any previous claim wherein said food casing is a self-supporting cellulosic food casing.
- 15 9. A cellulosic food casing according to claims 1 to 7 wherein said food casing is a reinforced cellulosic food casing.
10. A cellulosic food casing according to any previous claim which is a tubular food casing.
- 20 11. A cellulosic food casing according to claim 10 wherein said food casing is a tubular casing and said cellulose solution, having incorporated therein an optical property modifier, forms a portion on the outside of said casing.
- 25 12. A cellulosic food casing according to claim 10 or claim 11 provided with annular sectional regions, longitudinal substantially parallel striped regions

and/or longitudinal substantially helical striped regions incorporating said optical property modifier.

5 13. A process for manufacturing an optically modified cellulosic food casing which comprises a particulate material comprising the steps of

- providing a derivatised or non-derivatised cellulose solution;
- adding a particulate material to said solution to form a dispersion of particles in said solution; and
- 10 - extruding said solution through a die orifice.

15 14. The process according to claim 13 wherein said particulate material is added by mixing said particulate material with cellulose and/or NMMO, or by adding said particulate material to a solubilised cellulose-NMMO mixture.



INVESTOR IN PEOPLE

Application No: GB 0004737.3
Claims searched: 1-14

Examiner: Peter Trickey
Date of search: 3 August 2001

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): A2B (BAFDB)

Int Cl (Ed.7): A22C 13/00, 17/10

Other: Online: EPODOC, WPI, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0473952 A2 (Viskase) See Figure 3-6 and page 6 lines 28-31, 49-51, and 55-56 and page 8 lines 17-29 and 41-48	1-3, 8-14
X	EP 0373286 A1 (Viskase) See Figure 5 and page 4 lines 20-25	1, 8-12
A	US 5277857 A (Nicholson) See entire document	3
X	US 4336828 A (Balser) See entire document	1-2, 4

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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